Electrochemical Syntheses. III. The Homolytic Methoxylation of Some Arylated Olefins by the Anodic Oxidation of Methanol

By Tadao INOUE and Shigeru TSUTSUMI

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A method for the electrochemical methoxylation of furans has been developed.[1-3] Recently, Belleau and Weinberg[4] have reported the anodic methoxylation of dimethoxybenzenes and the ring fission of 1, 2-dimethoxybenzenes.

In the previous papers in this series,[5,6] we have described how the anodic oxidation of methanol in the presence of alkylated aromatic hydrocarbons produces α-methoxy derivatives, which are formed by the reaction of the methoxy radical generated by the electrolysis of methanol as an intermediate.

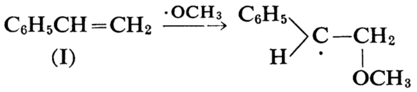
The present investigation was undertaken in order to study the addition of the methoxy radical to olefinic double bonds. Thus, styrene, α-methylstyrene and 1, 1-diphenylethylene were chosen as the starting olefins.

Results and Discussion

The Addition of the Methoxy Radical to Styrene.—According to the procedure described earlier,[5-6] the electrolysis of a methanol solution containing sodium methoxide was carried out in the presence of styrene (I) at 34°C; styrene glycol dimethyl ether (II) was obtained as a main proudct (current yield, 16—22%). The formation of α-methoxyethylbenzene (III) and β-methoxyethylbenzene (IV) as by-products was observed; *meso*-1, 4-dimethoxy-2, 3-diphenylbutane (V) was also isolated from the higher boiling fractions, and in addition a small amount of formaldehyde was isolated as its 2, 4-dinitrophenylhydrazone. The results obtained under various conditions are summarized in Table I, where the yield is calculated from the results of gas chromatographic analysis.

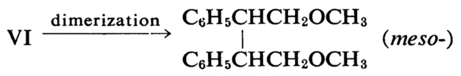
Since the methoxy radical may be initially produced as an intermediate in these reaction systems, it was expected that the reaction of methoxy radicals with styrene might take place in the first step of the reaction. The formation of *meso*-1, 4-dimethoxy-2,3-diphenylbutane (V) may be due to the coupling of an unstable intermediate radical (VI), which may be produced by the attack of the methoxy radical, formed by the anodic oxidation of methoxide ion, upon styrene, as is shown below:

$$CH_3O^- \xrightarrow[\text{anode}]{-e} CH_3O\cdot \qquad (1)$$



$$C_6H_5CH{=}CH_2 \xrightarrow{\cdot OCH_3} (C_6H_5)(H)\dot{C}{-}CH_2OCH_3 \qquad (2)$$

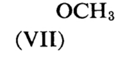
(I) (VI)



$$VI \xrightarrow{\text{dimerization}} \begin{array}{l} C_6H_5CHCH_2OCH_3 \\ \quad | \\ C_6H_5CHCH_2OCH_3 \end{array} \quad (meso\text{-}) \qquad (3)$$

(V)

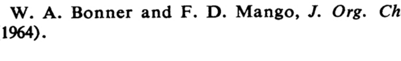
For the formation of styrene glycol dimethyl ether (II), two reaction paths are possible: In the first, the benzylic intermediate radical (VI) reacts with another methoxy radical to give the dimethyl ether (II), since the environment around the electrode might have a particularly high concentration of the methoxy radical (Eq. 4):



$$VI \xrightarrow{\cdot OCH_3} \begin{array}{ll} C_6H_5CH & {-}CH_2 \\ \quad | & \quad | \\ OCH_3 & OCH_3 \end{array} \qquad (4)$$

(II)

In the second, the intermediate radical (VI) may be oxidized to the carbonium ion (VII) to give the solvolysis product (II) (Eq. 5):



$$VI \xrightarrow[\text{anode}]{-e} \begin{array}{l} C_6H_5\overset{+}{C}H{-}CH_2 \\ \qquad\quad | \\ \qquad OCH_3 \end{array} \xrightarrow{^-OCH_3} II \qquad (5)$$

(VII)

Recently, Bonner and Mango[7] reported that electrolytically-generated benzyl radicals in the Kolbe elctrolysis are oxidized to carbonium ions with greater ease. Such a possibility can not be excluded in the present case.

For the anodic methoxylation of furan-compounds, Clauson-Kaas and his coworkers[1-3]

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[1] N. Clauson-Kaas, F. Limborg and K. Glens, *Acta Chem. Scand.*, **6**, 531 (1952).

[2] N. Clauson-Kaas and Z. Tyle, ibid., **6**, 667 (1952).

[3] N. Elming, " Advances in Organic Chemistry," Vol. II, Interscience Publ., New York (1960), p. 67.

[4] B. Belleau and N. L. Weinberg, *J. Am. Chem. Soc.*, **85**, 2525 (1963).

[5] T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1659 (1963).

[6] T. Inoue, K. Koyama and S. Tsutsumi, This Bulletin, in press.

[7] W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430 (1964).

TABLE I. ANODIC METHOXYLATION OF STYRENE

Expt.* No.	$C_6H_5CH=CH_2$ g. (mol.)	CH_3OH g.	Current density amp./dm^2	Amp.	Amp.-hr.	hr.	Product II g. (%**)	III g.	IV g.	V g.	Residue g.
1	50 (0.48)	75	18.8—13.3	2.2—1.6	24.4	12	16 (22.1)	0.9	trace	0.7	5.4
2	26 (0.25)	80	16.6	2.0	13.4	6.7	6.3 (15.1)	0.5	trace	0.4	3.2
3	52 (0.5)	80	16.6	2.0	26.8	13.4	15.2 (18.3)	1.2	trace	0.8	6.0
4	52 (0.5)	80	8.3	1.0	26.8	26.8	16.8 (20.0)	1.3	trace	0.8	4.5

* In these electrolyses, 1.0 g. of metallic sodium was used and the electrodes, 2×3 cm^2, were used; temperature being kept at 34±1°C.

** The current yields are based on the calculation that two moles of methanol should be oxidized to a one mole of the product II.

TABLE II. ANODIC METHOXYLATION OF ARYLATED OLEFINS

Expt.* No.	$C_6H_5CR=CH_2$ g. (mol.)		CH_3OH g.	Metallic sodium g.	Current density amp./dm^2	Amp.	Amp.-hr.	hr.	Product Dimethyl ether	g. (%)$^{a)}$	(%)$^{b)}$
1	R=H	52 (0.5)	80	1.0	8.3	1.0	26.8	26.8	II	16.8 (20.0)	(32.3)
2	$R=CH_3$	59 (0.5)	80	1.0	8.3	1.0	26.5	26.6	VIII	13.7 (15.0)	(23.2)
3	$R=C_6H_5$	45 (0.25)	40	0.5	8.3	1.0	13.6	13.6	IX	13.8 (23.0)	(30.7)

a) Current yield. b) Based on the starting olefin.

* The temperature was kept at 34±1°C.

reported that the bromine which is formed during the electrolysis reacts immediately with furan-compounds and methanol to give the methoxylated products and hydrogen bromide. On the other hand, in the present system, the anodic methoxylation of these olefins would proceed in the radical mechanisms, as has been mentioned above. This is also supported by the recent observation that the anodic oxidation of methanol in the presence of 1,2-dimethoxybenzene gives 5,5,6,6-tetramethoxy-1,3-cyclohexadiene under modified conditions.[4]

β-Methoxyethylbenzene (IV) might be produced by the hydrogen abstraction of the intermediate radical (VI) from the solvent:

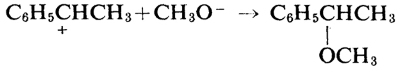
$$\text{VI} \xrightarrow{CH_3OH} C_6H_5CH_2CH_2OCH_3 \qquad (6)$$

(IV)

One possible rationalization for the formation of α-methoxyethylbenzene (III) in this system involves, in the first step, the addition of adsorbed hydrogen, which may be produced by the anodic oxidation of methoxide ions, as has been reported by Buck and Griffith,[8] to styrene; then methanolysis of the subsequent benzylic cation may furnish the methoxylated product (III), as is shown in Eqs. 7—9;

$$CH_3O^- \rightarrow CH_2O^-_{\text{adsorbed}} + H_{\text{adsorbed}} \qquad (7)$$

$$C_6H_5CH=CH_2 + H_{\text{adsorbed}} \rightarrow C_6H_5\underset{+}{C}HCH_3 + e \qquad (8)$$

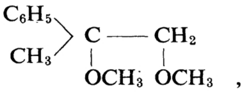


$$C_6H_5\underset{+}{C}HCH_3 + CH_3O^- \rightarrow C_6H_5\underset{\displaystyle OCH_3}{\underset{|}{C}}HCH_3 \qquad (9)$$

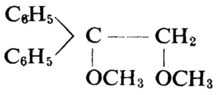
(III)

We have little experimental evidence, however, bearing on the validity of this suggestion.

The Addition of the Methoxy Radical to α-Methylstyrene and 1,1-Diphenylethylene.—When α-methylstyrene or 1,1-diphenylethylene was used instead of styrene, 1-methyl-1-phenylethylene glycol dimethyl ether (VIII) (current yield, 15%) or 1,1-diphenylethylene glycol dimethyl ether (IX) (current yield, 23%) was obtained as the main product in each case.



(VIII)



(IX)

The structure of these products was confirmed by the synthetic route. α-Methylstyrene glycol (X), which had been prepared by hydroxylation with a Milas-reagent,[9] and 1,1-diphenylethylene glycol (XI), prepared by the reaction of benzoylcarbinol with phenylmagnesium bromide,[10] were treated with n-butyl lithium and dimethyl sulfate successively in dry benzene to give the corresponding dimethyl ethers, which showed infrared absorptions and melting points identical

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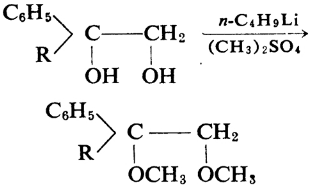
[8] R. P. Buck and L. R. Griffith, *J. Electro. Chem. Soc.*, **109**, 1005 (1962).

[9] N. A. Milas and S. Sussmann, *J. Am. Chem. Soc.*, **58**, 1302 (1936).

[10] S. H. Harper, "Chemistry of Carbon Compounds," Coll. Vol. IIIB, Elsevier Publ. Co., New York (1956), p. 1121.

with those of the electrochemical methoxylated products.



(10)

R=CH_3- (X), C_6H_5- (XI)

The results obtained are summarized in Table II. In these electrolyses, small amounts of the respective mono-ethers were also detected; white crystals which might be formed by the dimerization of an unstable intermediate radical were also isolated, as has been observed above. In the case of α-methylstyrene, in addition, a small amount of acetophenone was isolated as its 2, 4-dinitrophenylhydrazone.[11]

The current yields of these main products increased in the order $CH_3- < H- < C_6H_5-$ in the α-substituent group of styrene, as is shown in Table II.

It is of interest to note that the dimethyl ether derivatives (II, VIII and IX) are easily produced in fairly high yields by the anodic oxidation of methanol in the presence of the respective arylated olefins.

Experimental

Melting points and boiling points are uncorrected. Electrolyses were carried out by using three platinum-foil electrodes with the apparatus previously described.[5]

Materials.—Styrene and α-methylstyrene were commercial materials, carefully purified in the usual manner,[12] distilled before use, and stored in an ice-box. 1, 1-Diphenylethylene was obtained by the dehydration of the alcohol formed by the action of phenylmagnesium bromide and ethyl acetate;[13] b. p. 97—97.5°C/0.5 mmHg, $n_D^{15}=1.6098$. Methanol was purified in a manner described earlier.[5] These materials were confirmed to be pure by gas chromatography.

The Anodic Oxidation of Methanol in the Presence of Styrene.—The reaction conditions and the yields of the products are summarized in Table I.

R-4 is exemplified as follows: Metallic sodium (1.0 g., 0.043 mol.) was dissolved in 80 g. of absolute methanol (2.5 mol.), and then 52 g. of freshly-distilled styrene (0.5 mol.) was added to the mixture. After dry nitrogen had been bubbled through the mixture for about 1 hr., the mixture was electrolyzed at 34±1°C for 26.8 hr., during which time a current was maintained at neary 1.0 amp. (current density, 8.3 amp./dm^2). The electrolyzed solution turned slightly yellowish-brown. The reaction mixture was then distilled at room temperature under 25—30 mmHg pressure (water-aspirator). From this distillate, trapped by the receiver in a bath containing dry-ice and acetone, a small amount of formaldehyde was identified as its 2, 4-dinitrophenylhydrazone; m. p. 161—162°C; a mixed melting point with an authentic sample showed no depression.

Found: C, 40.22; H, 3.12; N, 26.80. Calcd. for $C_7H_6N_4O_4$: C, 40.00; H, 2.87; N, 26.62%.

The residue was poured into water (50 ml.), neutralized with 3 N hydrochloric acid, and extracted with ether; the extract was dried over magnesium sulfate. After the ether had been removed, the oily residue (49.5 g.) was distilled under diminished pressure to give the following fractions;

Fraction	B. p.	Weight, g.
1	~ 51°C/25 mmHg	18.3
2	30— 90°C/2—3 mmHg	21.1
3	90—103°C/2—3 mmHg	3.6
4	~143°C/0.8—0.9 mmHg	4.0
5	Residue	1.5

By gas chromatographic analysis (conditions: column, polyethylene glycol (P. E. G.) 1500, 2 m. and polyester D A (P. E. DA), 3 m.; column temperature, 153°C; carrier gas, H_2), it was shown that fractions 1, 2 and 3 were mixtures of unreacted styrene, α-methoxyethylbenzene, β-methoxyethylbenzene and styrene glycol dimethyl ether, and that the total amounts of these products were as follows: unreacted styrene, 23.0 g.; α-methoxyethylbenzen, 1.3 g.; β-methoxyethyl benzene, trace; styrene glycol dimethyl ether, 16.8 g.

Fraction 2 was chromatogroaphed over active alumina (2.5×58 cm.). Elution with benzene led to the isolation of styrene glycol dimethyl ether; b. p. 75—76°C/2 mmHg, $n_D^{20}=1.4948$ (lit.,[14] $n_D^{20}=1.4948$).

Found: C, 72.49; H, 8.79. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.

The infrared spectrum of this product showed the characteristic absorption band at 1105 cm^{-1} (C-O-C of aliphatic ether.) and was identical with that of an authentic sample prepared as will be described below.

α-Methoxyethylbenzene and β-methoxyethylbenzene were identified by gas chromatographic analysis.

Fraction 4 was cooled below 0°C to give a white crystal (0.6 g.) of *meso*-1, 4-dimethoxy-2, 3-diphenylbutane (m. p. 128.5-130°C) from methanol; a mixed melting point with the sample prepared as will be described below showed no depression.

Found: C, 80.07; H, 8.19. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%.

The infrared spectrum of this compound showed the characteristic absorption band at 1112 cm^{-1} (C-O-C). The mother liquid filtered from fraction 4 was chromatographed over active alumina (2.5×30 cm.) and, from the eluate with benzene, 0.2 g. of *meso*-1, 4-dimethoxy-2, 3-diphenylbutane and oily compounds were separated. The latter oily compounds consisted of miscellaneous products, which

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[11] For the formation of this ketone, further studies are now being undertaken.

[12] A. Weissberger, "Technique of Organic Chemistry," Vol. VII, Interscience Publ., New York (1955), p. 331.

[13] "Organic Syntheses," Coll. Vol. I, 226 (1956).

[14] C. R. Ganellin and R. Pettit, *J. Chem. Soc.*, **1958**, 576.

showed the infrared absorption band at 1110 cm^{-1} (C-O-C); b. p. 130—170°C/2—3 mmHg.

The Synthesis of Styrene Glycol Dimethyl Ether.—Styrene diacetate was prepared by the reaction of styrene dibromide with fused lead acetate in glacial acetic acid, according to the procedure of Evans and Morgan;15) b. p. 126—128°C/4—5 mmHg. Styrene glycol was prepared by the hydrolysis of styrene diacetate14) and was methylated with methyl sulfate as has been described for glucose;16) b. p. 72—73°C/1.5 mmHg, $n_D^{20}=1.4948$.

The Synthesis of *α*- and *β*-Methoxyethylbenzene.—*α*-Methoxyethylbenzene was prepared by the reaction of styrene with methanol according to the procedure of Stanley and was then purified by preparative gas chromatography;5) b. p. 74—75°C/30—32 mmHg, $n_D^{22}=1.4900$. *β*-Methoxyethylbenzene was prepared by the reaction of phenethyl alcohol with metallic sodium and methyl iodide; b. p. 46—47°C/3—4 mmHg.

The Synthesis of *meso*-1, 4-Dimethoxy-2, 3-diphenylbutane.—*meso*-2, 3-Diphenyl-1, 4-butanediol17) was prepared by the reduction, with lithium aluminum hydride, of *meso*-diethyl *α*, *α'*-diphenylsuccinate,18) which had been synthesized by the coupling of ethyl phenylacetate19) with sodium ethoxide and iodine; m. p. 143—144°C (lit., m. p. 143—144°C). *meso*-1, 4-Dimethoxy-2, 3-diphenylbutane was prepared by the following procedure: *meso*-2,3-diphenyl-1, 4-butanediol (1.5 g., 0.006 mol.) was dissolved in 60 ml. of dry benzene, and then the solution was further dried by the distillation of 10 ml. of benzene. To the solution at room temperature, 6 ml. of *n*-butyl lithium in *n*-heptane (21% solution, 0.015 mol.) was added, and then the solution was stirred at 60°C for 1.5 hr. Dimethyl sulfate (3.78 g., 0.03 mol.) in 20 ml. of dry benzene was then added, and the solution was heated at 80°C for 8 hr., cooled in ice, transferred to an amber separatory funnel, and washed successively with a cold solution of 0.5 N sulfuric acid (100 ml.), N ammonium hydroxide (twice) and water (three times). The solution was dried over anhydrous sodium sulfate, filtered, concentrated at 40°C under reduced pressure, and cooled to give crystals (1.4 g., 85% yield) of *meso*-1, 4-dimethoxy-2, 3-diphenylbutane; m. p. 128.5—130°C, from methanol.

The Anodic Oxidation of Methanol in the Presence of *α*-Methylstyrene.—Metallic sodium (1.0 g., 0.043 mol.) was dissolved in 80 g. of absolute methanol (2.5 mol.). and then 59 g. of freshly-distilled *α*-methylstyrene (0.5 mol.) was added to the mixture. After dry nitrogen had been bubbled through the mixture, the mixture was electrolyzed at 34±1°C, for 26.6 hr. during which time the current was maintained at 1.0 amp. The reaction mixture was then worked up in a manner similar to the procedure described above. After the ether had been removed, the oily residue was distilled under reduced pressure to give the following fractions;

Fraction	B. p.	Weight, g.
1	∼ 40°C/2—3 mmHg	20.6
2	40— 55°C/2—3 mmHg	8.8
3	55—105°C/2—3 mmHg	22.3
4	Residue	5.3

Gas chromatographic analysis (conditions: column, polyester DA, 3 m. and polyethylene glycol 6000, 3 m.; column temperature, 173°C; carrier gas, H_2) showed that fractions 1, 2 and 3 were mixtures of unreacted *α*-methylstyrene, *α*-methoxyisopropylbenzene, acetophenone, *β*-methoxyisopropylbenzene and 1-methyl-1-phenylethylene glycol dimethyl ether, and that the total amounts of these products were as follows: unreacted *α*-methylstyrene, 33.7 g.; *α*-methoxyisopropylbenzene, 2.2 g.; acetophenone, 3.2 g; *β*-methoxyisopropylbenzene, trace; 1-methyl-1-phenylethylene glycol dimethyl ether, 13.7 g.

When fraction 3 was distilled through a five-foot vacuum-jacketed column packed with glass helices, 1-methyl-1-phenylethylene glycol dimethyl ether was isolated; b. p. 68—69°C/1.5 mmHg, $n_D^{14}=1.5022$.

Found: C, 73.59; H, 9.20. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

The infrared spectrum of this dimethyl ether showed the characteristic absorption bands at 1110 cm^{-1} and 1128 cm^{-1} (C-O-C) and was identical with that of an authentic sample prepared as will be described below. From the lower boiling fraction, acetophenone was identified as its 2, 4-dinitrophenylhydrazone derivative; m. p. 237—238°C; a mixed melting point with an authentic sample was not depressed.

Found: C, 56.17; H, 3.93. Calcd. for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03%.

α-Methoxyisopropylbenzene and *β*-methoxyisopropylbenzene were identified by gas chromatographic analysis (conditions; described above). When fraction 4, the residue, was chromatographed over active alumina (2.5×45 cm.) and eluted with benzene, a white crystal (0.1 g. with m. p. 95—96.5°C, from methanol), was isolated from oily miscellaneous products.

Found: C, 80.36; H, 8.89. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78%.

The infrared spectrum of this compound showed the characteristic absorption bands at 1088 cm^{-1} and 1098 cm^{-1} (C-O-C).

The Synthesis of 1-Methyl-1-phenylethylene Glycol Dimethyl Ether.—1-Methyl-1-phenylethylene glycol was prepared by the action of Milas reagents on *α*-methylstyrene9) and methylated in a good yield with *n*-butyl lithium and dimethyl sulfate in dry benzene in a manner similar to the procedure described above. The product had a b. p. of 66°C/1 mmHg, $n_D^{14}=1.5022$.

The Synthesis of *α*- and *β*-Methoxyisopropylbenzene.—*α*-Methoxyisopropylbenzene was synthesized in a manner described earlier;5) b. p. 77—78°C/12—13 mmHg, $n_D^{20}=1.4911$. *β*-Methoxyisopropylbenzene was synthesized by the *O*-methylation of *β*-phenylpropyl alcohol with *n*-butyl lithium and dimethyl sulfate in a manner similar to the

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15) W. L. Evans and L. H. Morgan, *J. Am. Chem. Soc.*, **35**, 54 (1913).

16) "Organic Syntheses," Coll. Vol. III, 800 (1955).

17) F. F. Blicke, P. E. Wright and W. A. Gould, *J. Org. Chem.*, **26**, 2114 (1961); D. Fraenkel and P. Bartlett, *J. Am. Chem. Soc.*, **81**, 5582 (1959).

18) H. Wren and C. J. Still, *J. Chem. Soc.*, **1915**, 446.

19) "Organic Syntheses," Coll. Vol. I, 270 (1956).

procedure as described above; b. p. 85—86°C/14 mmHg. β-Phenylpropyl alcohol was prepared by the reduction of β-phenylpropionaldehyde, which was prepared by the dehydration of 1-methyl-1-phenylethylene glycol with 20% sulfuric acid,[20] with zinc and acetic acid[21]; b. p. 99—102°C/7—8 mmHg.

The Anodic Oxidation of Methanol in the Presence of 1, 1-Diphenylethylene.—Metallic sodium (0.5 g., 0.022 mol.) was dissolved in 40 g. of methanol (1.25 mol.), and then 45 g. of freshly-distilled 1, 1-diphenylethylene (0.25 mol.) was added to the mixture. After dry nitrogen had been bubbled through the cell, the mixture was electrolyzed at 34±1°C, for 13.8 hr., during which time the current was maintained at 1.0 amp. The electrolyzed solution was worked up in a manner similar to the procedure described above, and the oily residue (50.0 g.) was distiiled under reduced pressure to give the following fractions;

Fraction	B. p.	Weight, g.
1	90— 99°C/1.0 mmHg	22.5
2	99—125°C/1.0 mmHg	23.5
3	Residue	3.0

These fractions were chromatographed over active alumina (2.5×26 cm.). Elution with benzene led to the isolation of unreacted 1, 1-diphenylethylene (31.4 g.), 1, 1-diphenylethylene glycol dimethyl ether (13.8 g.), miscellaneous oily products (4.5 g.) and a white crystal (0.4 g.) with a m. p. of 228—230°C, from benzene.

1, 1-Diphenylethylene glycol dimethyl ether was melted at 65.5—66.5°C from ligroin; a mixed melting point with the sample prepared as will be described below showed no depression.

Found: C, 79.06; H, 7.25. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

The infrared spectrum of this dimethyl ether showed the characteristic absorption bands at 1108 cm^{-1} and 1138 cm^{-1} (C-O-C) and was identical with that of the sample prepared as will be described below. The infrared spectrum of a white crystal with a m. p. of 228.5—230°C also showed the characteristic absorption band at 1072 cm^{-1} (C-O-C).

Found: C, 85.53; H, 7.41. Calcd. for $C_{30}H_{30}O_2$: C, 85.27; H, 7.16%.

The Synthesis of 1, 1-Diphenylethylene Glycol Dimethyl Ether. — Benzoylcarbinol[22] was prepared by the hydrolysis of benzolycarbinol acetate prepared by the reaction of ω-bromoacetophenone with potassium acetate;[22] m. p. 80—82°C. 1, 1-Diphenylethylene glycol was prepared by the treatment of benzoylcarbinol with phenylmagnesium bromide;[10] m. p. 119—120.5°C (lit.,[10] m. p. 121°C), and methylated in a good yield with *n*-butyl lithium and dimethyl sulfate in dry benzene in a manner similar to the procedure described above. The product was purified by column chromatography (active alumina, 2.5×26 cm.; eluted with benzene); m. p. 65.5—66.5°C, from ligroin.

Department of Chemical Technology
Faculty of Engineering
Osaka University
Miyakojima-ku, Osaka

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[20] S. Danilow and E. Venus-Danilowa, *Ber.*, **60**, 1063 (1927).

[21] J. B. Cohen, J. Marshall and H. E. Woodman, *J. Chem. Soc.*, **107**, 887 (1915).

[22] W. Madelung and M. E. Oberwegner, *Ber.*, **65**, 931 (1932).